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[Name of Document] Claims 1

[Name of Document] CLAIMS

[Claim 1] A method for manufacturing a monocrystalline thin film, comprising the steps of;

(a) preparing a monocrystalline substrate;

(b) forming a sacrificial layer containing crystal defects on the monocrystalline substrate using the same material by epitaxial growth;

(c) forming a monocrystalline thin film containing crystal defects on the sacrificial layer using the same material by epitaxial growth, the number of the crystal defects being smaller than that of the sacrificial layer; and

(d) etching the sacrificial layer so as to form a monocrystalline thin film containing a small number of crystal defects.

[Claim 2] The method for manufacturing a monocrystalline thin film, according to Claim 1, further comprising the step of eliminating crystal defects present on the surface of the sacrificial layer following the step (b).

[Claim 3] The method for manufacturing a monocrystalline thin film, according to Claim 1 or 2, wherein the monocrystalline substrate is a monocrystalline silicon substrate, the sacrificial layer is a silicon sacrificial layer, and the monocrystalline thin film is a

high (see Patent Document 1 below).

(b) Hydrogen Ion Implantation Method

After hydrogen ions (H+ and H-) are implanted into a monocrystalline silicon substrate, this substrate is adhered to a support substrate, followed by heat treatment. Subsequently, a layer implanted with the hydrogen ions is destroyed and is then peeled away, so that a monocrystalline silicon thin film having a thickness on the order of submicrons can be formed on the support substrate.

[0004]

Since implanted hydrogen can only reach a depth on the order of submicrons, for example, in solar cell applications, the thickness of the monocrystalline silicon thin film must be increased to approximately 10 μm by a chemical vapor deposition or a physical vapor deposition method at a temperature of 1,000°C or more. However, it is difficult to obtain an inexpensive substrate which can satisfy requirements for heat resistance and coefficient of thermal expansion. In addition, a method for increasing the thickness of a monocrystalline silicon thin film before a hydrogen ion implanted layer is peeled away from a substrate cannot be realized since the hydrogen ion implanted layer is destroyed under the film-thickening conditions (see Patent Document 2 below).

(c) Porous Silicon Method

[Claim 9] The method for manufacturing a monocrystalline thin film, according to one of Claims 3 and 6 to 8, wherein twins exist at the boundary between the monocrystalline silicon substrate and the silicon sacrificial layer at a number density of 1/μm2 to 1/nm2.

[Claim 10] The method for manufacturing a monocrystalline thin film, according to one of Claims 3 and 6 to 9, further comprising, following the step (b), the step of performing thermal annealing in a reducing atmosphere at a temperature of 1,000 to 1,400°C to eliminate crystal defects on the surface of the silicon sacrificial layer.

[Claim 11] The method for manufacturing a monocrystalline thin film, according to Claim 10, wherein after the thermal annealing, the number density of twins present on the surface of the silicon sacrificial layer is one hundredth or less of that of twins present at the boundary between the monocrystalline silicon substrate and the silicon sacrificial layer.

[Claim 12] The method for manufacturing a monocrystalline thin film, according to one of Claims 3 and 6 to 11, wherein the step (c) is performed by a physical vapor deposition method or a chemical vapor deposition method at a temperature of 1,000 to 1,400°C, whereby the monocrystalline silicon thin film containing a small number of crystal defects is formed by epitaxial growth.

of steps are required, and the process is also disadvantageously complicated.

(d) Melting Recrystallization Method/Melting Crystallization Method

When a silicon dioxide film, a polycrystalline or an amorphous silicon thin film, and a protective layer made of silicon dioxide are laminated in that order on a silicon substrate, and scanning of a line-shaped melting zone by lamp heating or the like is performed, a polycrystalline silicon thin film can be formed in which crystal grains are well grown in the in-plane direction. Subsequently, after the protective layer is chemically dissolved, and the thickness of the polycrystalline silicon thin film is increased by a CVD method, etching of the silicon dioxide film is performed with hydrofluoric acid, so that the polycrystalline silicon thin film can be separated (see Patent Document 4 below).

[0006]

However, since the thin layer thus obtained is merely a polycrystalline silicon thin film, besides inferior energy conversion efficiency, the silicon substrate is also disadvantageously degraded while the molten zone is scanned, and in addition, the process is complicated due to a great number of manufacturing steps.

(e) Epitaxial Lift-Off (ELO) Method Using Sacrificial Layer

6 to 16, further comprising the step of forming a texture structure on the surface of the monocrystalline silicon substrate.

[Claim 18] The method for manufacturing a monocrystalline thin film, according to one of Claims 3 and 6 to 17, wherein the etching of the silicon sacrificial layer is performed using a mixed solution of hydrofluoric acid and an oxidizing agent.

[Claim 19] A monocrystalline thin film device obtained by the method for manufacturing a monocrystalline thin film, according to one of Claims 1 to 5.

[Claim 20] A monocrystalline thin film device obtained by the method for manufacturing a monocrystalline silicon thin film, according to one of Claims 3 and 6 to 18.

[Claim 21] The monocrystalline thin film device according to Claim 20, wherein the monocrystalline silicon thin film is a photovoltaic layer of solar-cells.

[Claim 22] The monocrystalline thin film device according to Claim 20, wherein the monocrystalline silicon thin film is a monocrystalline silicon thin film used for SOI.

[Patent Document 2] Japanese Unexamined Patent Application Publication No. 11-040785

[Patent Document 3] Japanese Unexamined Patent Application Publication No. 05-275663

[Patent Document 4] Japanese Unexamined Patent Application Publication No. 07-226528

[Patent Document 5] WO0240751

[Disclosure of Invention]

[Problems to be Solved]

[0008]

The above-described epitaxial lift-off method (e) using a sacrificial layer having a different elemental composition will be further described in detail, and in addition, problems of this method will also be described.

[0009]

Fig. 13 includes cross-sectional views (part 1) showing a process for manufacturing a monocrystalline silicon film by the epitaxial lift-off method described above which uses a sacrificial layer having a different elemental composition.

[0010]

(1) First, a monocrystalline silicon substrate 1 is prepared as shown in Fig. 13(a).

[0011]

(2) Next, as shown in Fig. 13(b), on the surface of the monocrystalline silicon substrate 1, a metal silicide (MSi

[0017]

(3) Next, as shown in Fig. 14(c), on the surface of the highly doped silicon film 12, a monocrystalline silicon film 13 is epitaxially-grown.

[0018]

(4) Subsequently, as shown in Fig. 14(d), the highly doped silicon film 12 is removed by etching, so that the monocrystalline silicon film 13 is separated.

[0019]

However, according to the methods for manufacturing a monocrystalline silicon film described above, there have been the following problems.

[0020]

(A) According to the above-described method for manufacturing a monocrystalline silicon film shown in Fig. 13,

when the metal silicide (CoSi2, NiSi2, or CrSi2) film 2 is used as the sacrificial layer, selective etching of this metal silicide film 2 can be easily performed with an aqueous HF solution as an etching agent; however, metal atoms are incorporated into the monocrystalline silicon film 3, and hence a high-purity monocrystalline silicon film cannot be manufactured.

[0021]

(B) According to the above-described method for

monocrystalline layer containing crystal defects which is formed from the same elemental composition as the sacrificial layer. For example, in manufacturing of a monocrystalline silicon thin film, when silicon is grown on a monocrystalline silicon substrate in an atmosphere containing small amounts of oxygen and water vapor, a silicon layer is being epitaxially-grown as a whole; however, crystal defects such as twins may be included in the silicon layer. Subsequently, when thermal annealing is performed in a reducing atmosphere (hydrogen atmosphere), because of surface diffusion of silicon, defects on the topmost surface are eliminated. When silicon is grown thereon under clean conditions in which crystal defects are not formed, a structure can be formed composed of a monocrystalline silicon thin film/monocrystalline silicon sacrificial layer containing crystal defects/monocrystalline silicon substrate. Since a sacrificial layer containing crystal defects can be selectively etched with a mixed solution containing hydrofluoric acid and an oxidizing agent, the lift-off can be preferably performed, and in addition, a high-purity monocrystalline silicon thin film can be obtained.

[0024]

The method of the present invention would be a high-potential process because it does not lead to the incorporation of elements, which decreases the energy

In addition, the apparent problem, that is, shortage of high-purity silicon, can also be solved. Furthermore, when the cost can be reduced to a level competitive to a system power source, the use of solar cells may widely spread without having any political support, and significant expansion of solar cell market can be expected.

[Best Mode for Carrying Out the Invention]

[0029]

Hereinafter, embodiments of the present invention will be described in detail.

[0030]

(1) Fig. 1 includes cross-sectional views (part 1) showing manufacturing steps of a monocrystalline thin film of an example according to the present invention.

[0031]

First, as shown in Fig. 1(a), a monocrystalline substrate 21 is prepared. Next, as shown in Fig. 1(b), a monocrystalline sacrificial layer 22 containing crystal defects is epitaxially-grown using the same material as that of the monocrystalline substrate 21. Then, as shown in Fig. 1(c), a high-purity monocrystalline thin film 23 is epitaxially-grown on this monocrystalline sacrificial layer 22 using the same material as that thereof. Subsequently, as shown in Fig. 1(d), the monocrystalline sacrificial layer 22 is etched (dissolved), and as a result, the high-purity

Also in this case, the remaining monocrystalline substrate 31 shown in Fig. 2(e) can be reused.

[0036]

(3) Fig. 3 includes cross-sectional views (part 3) showing manufacturing steps of a monocrystalline thin film of an example according to the present invention.

[0037]

First, as shown in Fig. 3(a), a monocrystalline substrate 41 is prepared. Next, as shown in Fig. 3(b), a monocrystalline sacrificial layer 42 containing crystal defects is epitaxially-grown using the same material as that of the monocrystalline substrate 41. Then, as shown in Fig. 3(c), a high-purity monocrystalline thin film 43 is epitaxially-grown on this monocrystalline sacrificial layer 42 using the same material as that thereof. Subsequently, as shown in Fig. 3(d), the high-purity monocrystalline thin film 43 is supported by a support base material 44. Next, as shown in Fig. 3(e), the monocrystalline sacrificial layer 42 is etched (dissolved), and as a result, the high-purity monocrystalline thin film 43 supported by the support base material 44 is manufactured.

[0038]

Also in this case, the remaining monocrystalline substrate 41 shown in Fig. 3(e) can be reused.

[0039]

[0042]

(5) In the method for manufacturing a monocrystalline thin film according to one of the above (1) to (4), the monocrystalline substrate is a monocrystalline silicon substrate, the sacrificial layer is a silicon sacrificial layer, and the monocrystalline thin film is a monocrystalline silicon thin film.

[0043]

(6) In the method for manufacturing a monocrystalline thin film, according to one of the above (1) to (4), the monocrystalline substrate is a monocrystalline GaAs substrate.

[0044]

(7) In the method for manufacturing a monocrystalline thin film, according to one of the above (1) to (4), the monocrystalline substrate is an MgO substrate.

[0045]

(8) In the method for manufacturing a monocrystalline thin film, according to one of the above (1) to (4), the step (b) is performed by a physical vapor deposition method or a chemical vapor deposition method at a temperature of 400 to 1,200°C, so that a silicon sacrificial layer containing crystal defects is formed by epitaxial growth.

[0046]

(9) In the method for manufacturing a monocrystalline

Then, as shown in Fig. 5(d), under a second film-forming condition in which a remaining gas pressure is lower than that under the first film-forming condition and the temperature is high, a monocrystalline silicon thin film 64 containing a small number of defects is epitaxially-grown. Accordingly, as shown in Fig. 5(e), the monocrystalline silicon sacrificial layer 62 is etched (dissolved), and as a result, the high-purity monocrystalline silicon thin film 64 is manufactured.

[0050]

In addition, after being epitaxially-grown, the high-purity monocrystalline silicon film 64 which is supported by a support base material (not shown) may be manufactured by the steps of supporting the monocrystalline silicon film 64, which is located at an upper side, by the support base material and then etching (dissolving) the monocrystalline sacrificial layer 62.

[0051]

Also in this case, the remaining monocrystalline substrate 61 shown in Fig. 5(e) can be reused.

[0052]

(12) In the method for manufacturing a monocrystalline thin film, according to the above (2) or (4), following the step (b), thermal annealing is performed in a reducing atmosphere at a temperature of 1,000 to 1,400°C, so that

[0056]

(16) In the method for manufacturing a monocrystalline thin film, according to the above (3), holes are formed in the monocrystalline silicon substrate at intervals, so that etching of a monocrystalline sacrificial layer is easily performed.

[0057]

(17) In the method for manufacturing a monocrystalline thin film, according to the above (3), the thickness of the silicon sacrificial layer is set to 100 nm or less, so that roughness of the bottom surface of the monocrystalline silicon thin film is reduced to 100 nm or less.

[0058]

(18) In the method for manufacturing a monocrystalline thin film, according to the above (3), the thickness of the silicon sacrificial layer is set to 100 nm or more, so that the bottom surface of the monocrystalline silicon thin film has a texture structure of 100 nm or more.

[0059]

(19) In the method for manufacturing a monocrystalline thin film, according to one of the above (1) to (4), a texture structure is formed on the surface of the monocrystalline silicon substrate. Accordingly, in particular, it is intended to improve the energy conversion efficiency when the monocrystalline thin film is used as a

Fig. 6 includes cross-sectional views showing manufacturing steps of Example 1 according to the present invention.

[0066]

(1) First, as shown in Fig. 6(a), a monocrystalline silicon substrate (such as 500 μm thick) 71 is prepared.

[0067]

This monocrystalline silicon substrate 71 has a flat upper surface since a monocrystalline silicon sacrificial film, which will be described later, is to be epitaxially-grown.

[0068]

(2) Next, as shown in Fig. 6(b), on the monocrystalline silicon substrate 71, by a sputter-deposition method with substrate heating, silicon containing crystal defects is epitaxially-grown in an atmosphere containing small amounts of oxygen and water vapor. That is, a monocrystalline silicon sacrificial film (such as 0.1 to 1 μm thick) 72 containing crystal defects is formed. This monocrystalline silicon sacrificial film 72 can be easily and precisely removed by etching, as described later.

[0069]

(3) Next, as shown in Fig. 6(c), on the monocrystalline silicon sacrificial film 72, monocrystalline silicon containing a small number of defects is epitaxially-grown by

substrate 71 by epitaxial growth using a sputter-deposition method with substrate heating at a temperature of 600°C, then forming the monocrystalline silicon thin film 73 containing a small number of defects and having a thickness of 20 μm on the above sacrificial film by a chemical vapor deposition method at a temperature of 1,200°C using a mixture of trichlorosilane and a hydrogen gas as raw materials, and then etching a part of the sacrificial film 72 using a HF/HNO3/CH3COOH mixed solution. In the figure, the state is shown in which the sacrificial film 72 is selectively etched.

[Example 2]

[0073]

Fig. 8 includes cross-sectional views showing manufacturing steps of Example 2 according to the present invention.

[0074]

(1) First, as shown in Fig. 8(a), a monocrystalline silicon substrate (such as 500 μm thick) 81 is prepared.

[0075]

This monocrystalline silicon substrate 81 has a flat upper surface since a monocrystalline silicon sacrificial film, which will be described later, is to be epitaxially-grown.

[0076]

[0079]

(4) Next, as shown in Fig. 8(d), a support base material 84 is held on the monocrystalline silicon thin film 83. As the support base material 84, a reinforced glass may be used.

[0080]

(5) Next, as shown in Fig. 8(e), selective etching of the monocrystalline silicon sacrificial film 82 is performed using a HF/HNO3/CH3COOH mixed solution or a HF/KMnO4/CH3COOH mixed solution, so that the high-purity monocrystalline silicon thin film 83 is separated which contains a small number of defects and which is supported by the support base material 84.

[Example 3]

[0081]

Fig. 9 includes cross-sectional views showing manufacturing steps of a monocrystalline thin film of Example 3 according to the present invention.

[0082]

This example is the same as Examples 1 and 2 except that holes 91A are formed in a monocrystalline silicon substrate 91 at intervals. That is,

(1) first, as shown in Fig. 9(a), the monocrystalline silicon substrate 91 is prepared in which the holes 91A are provided at intervals.

the monocrystalline silicon sacrificial film 92 is performed using a HF/HNO3/CH3COOH mixed solution or a HF/KMnO4/CH3COOH mixed solution. In this case, since the etchant is likely to enter the holes 91A formed in the monocrystalline silicon substrate 91 at intervals, separation of the monocrystalline silicon thin film 93 having a small number of defects can be smoothly performed. That is, the monocrystalline silicon sacrificial film 92 can be rapidly and precisely removed.

[0088]

In this example, the formation of holes is applied to the manufacturing method of Example 2 and may also be applied to that of Example 1.

[0089]

In addition, by decreasing the thickness of the silicon sacrificial layer 92 to 100 nm or less, the roughness of the bottom surface of the monocrystalline silicon thin film 93 can be reduced to 100 nm or less.

[0090]

Alternatively, by increasing the thickness of the silicon sacrificial layer 92 to 100 nm or more, a texture structure of 100 nm or more may be formed on the bottom surface of the monocrystalline silicon thin film 93. In particular, when the monocrystalline silicon thin film is used as a photovoltaic layer of solar cells, sunlight can be efficiently brought into the monocrystalline thin film, and

containing small amounts of oxygen and water vapor. That is, a monocrystalline silicon sacrificial film 102 having the texture structure 102A on the surface thereof is formed.

[0095]

(3) Next, as shown in Fig. 11(c), on the monocrystalline silicon sacrificial film 102, monocrystalline silicon containing a small number of defects is epitaxially-grown by a CVD method. That is, a monocrystalline silicon thin film 103 containing a small number of crystal defects is formed which has a texture structure 103B on the front surface and a texture structure 103A on the rear surface.

[0096]

(4) Next, as shown in Fig. 11(d), a support base material 104 is held on the monocrystalline silicon thin film 103.

[0097]

(5) Next, as shown in Fig. 11(e), selective etching of the monocrystalline silicon sacrificial film 102 is performed using a HF/HNO3/CH3COOH mixed solution or a HF/KMnO4/CH3COOH mixed solution, so that the monocrystalline silicon thin film 103 is separated which is supported by the support base material 104 and which has the texture structure 103A on the front surface and the texture structure 103B on the rear surface.

monocrystalline thin film, and hence the energy conversion efficiency can be improved.

[0102]

The present invention is not limited to the examples described above, and various modifications may be performed without departing from the spirit and the scope of the present invention and may not be excluded therefrom.

[Industrial Applicability]

[0103]

The present invention is suitably applied, for example, to methods for manufacturing photovoltaic layers of solar cells and monocrystalline thin films of silicon and compound semiconductors used for semiconductor devices and to methods for manufacturing SOI substrates.

[Brief Description of the Drawings]

[0104]

[Fig. 1] Cross-sectional views (part 1) showing manufacturing steps of a monocrystalline thin film of an example according to the present invention.

[Fig. 2] Cross-sectional views (part 2) showing manufacturing steps of a monocrystalline thin film of an example according to the present invention.

[Fig. 3] Cross-sectional views (part 3) showing manufacturing steps of a monocrystalline thin film of an example according to the present invention.

of Example 4 according to the present invention.

[Fig. 13] Cross-sectional views (part 1) showing manufacturing steps of a monocrystalline silicon film by a conventional epitaxial lift-off method using a sacrificial layer having a different elemental composition.

[Fig. 14] Cross-sectional views (part 2) showing manufacturing steps of a monocrystalline silicon film by a conventional epitaxial lift-off method using a sacrificial layer having a different elemental composition.

[Description of Symbols]

[0105]

21, 31, 41, 51: monocrystalline substrate

22, 32, 42, 52: monocrystalline sacrificial layer

23, 34, 43, 54: high-purity monocrystalline thin film

33, 53: surface of monocrystalline sacrificial layer

44, 55, 84, 94, 104: support base material

61, 71, 81, 91, 101: monocrystalline silicon substrate

62, 72, 82, 92, 102: monocrystalline silicon sacrificial film

63: surface of monocrystalline silicon sacrificial film

64, 73, 83, 93, 103: monocrystalline silicon thin film

91A: hole

101A, 102A, 103A, 103B: texture structure

[Name of Document] ABSTRACT

[Abstract]

[Object] The present invention provides a method for manufacturing a monocrystalline film and a device formed by the above method, and according to the method mentioned above, lift-off of the monocrystalline silicon film is preferably performed and a high-purity monocrystalline silicon film can be obtained.

[Solving Means] A monocrystalline silicon substrate (template Si substrate) 201 is prepared, and on this monocrystalline silicon substrate 201, an epitaxial sacrificial layer 202 is formed. Subsequently, on this sacrificial layer 202, a monocrystalline silicon thin film 203 is rapidly epitaxially-grown using a RVD method, followed by etching of the sacrificial layer 202, whereby a monocrystalline silicon thin film 204 used as a photovoltaic layer of solar cells is formed.

[Selected Drawing] Fig. 6